

LISTING BACKGROUND DOCUMENT

Steel Finishing

Spent Pickle Liquor (C) (T)*

I. Summary of Basis for Listing:

Spent pickle liquor is generated in the pickling of iron and steel to remove surface scale. The Administrator has determined that spent pickle liquor is a solid waste which may pose a present or potential hazard to human health and the environment when improperly transported, treated, stored, disposed of, or otherwise managed, and, therefore, should be subject to appropriate management requirements under Subtitle C of RCRA. This conclusion is based on the following considerations:

1. Spent pickle liquor is corrosive (has been shown to have pH less than 2), and contains significant concentrations of the toxic metals lead and chromium.
2. The toxic metals in spent pickle liquor are present in highly mobile form, since it is an acidic solution. Therefore, these hazardous constituents are readily available to migrate from the waste in harmful concentrations, causing harm to the environment.

*In response to comments received by the Agency on the interim final list of hazardous waste (45 FR 33124, May 19, 1980), sludge from lime treatment of spent pickle liquor has been removed from the hazardous waste list (see Response to Comments at the back of this listing background document for more details).



3. Current waste management practices of untreated spent pickle liquor consist primarily of land disposal either in unlined landfills or unlined lagoons which may be inadequate to prevent the migration of lead and chromium to underground drinking water sources. Treatment of the spent pickle liquor by neutralization is also commonly practiced by the industry in which case, a lime treatment sludge is generated.
4. A very large quantity (approximately 1.4 billion gallons of spent pickle liquor) is generated annually. There is a great likelihood of large-scale contamination of the environment if these wastes are not managed properly.
5. Damage incidents have been reported that are attributable to the improper disposal of poorly treated spent pickle liquor.

II. Industry Profile and Process Description

Pickling operations are very widespread across the United States. Spent pickle liquor is generated at 240 plants located in 34 states. Approximately 70% of these plants are situated in Pennsylvania, Ohio, Illinois, Indiana and Michigan. Pickling capacity within the iron and steel industry, according to the type of acid used, is shown in Table 1 below.⁽¹⁾

The pickling operation involves the immersion of oxidized steel in a heated solution of concentrated acid or acids (the pickling agent) to remove surface oxidation or to impart specific surface characteristics. At integrated steel plants, acid pickle liquors are used in cold rolling mills and galvanizing mills. Depending on the type of steel being processed, or the type of surface quality desired, different types of acids may be used. For example, most carbon steels are pickled in sulfuric

or hydrochloric acids, while most stainless and alloy steels are pickled in a mixture of nitric and hydrofluoric acids.(1) After a certain concentration of metallic ions build up in the pickling bath, the solution is considered spent or exhausted and must be replaced.

Table 1

<u>Pickling Agent</u>	<u>Number of Plants*</u>	<u>Annual Capacity, tons of steel/yr</u>
HCl	43	30,000,000
H ₂ SO ₄	149	28,000,000
Mixed acid (e.g. HF-HNO ₃)	152	6,000,000

III. Waste Generation and Management

Approximately 1.4 billion gallons of spent pickle liquor are generated annually: 500 million gallons of spent sulfuric acid, 800 million gallons of spent hydrochloric acid, and 74 million gallons of a combination (mixed) of pickling acids.** When treated with lime, spent pickle liquors form a spent pickle liquor lime treatment sludge.

The spent pickle liquor is a strongly acid solution (pH <1) containing very high concentrations of dissolved iron, and

*If the same plant uses two or three pickling agents, it is listed once for each agent used.

**Estimates based on waste generation data contained in Reference 1.

significant amounts of many other metals, including chromium (26-4250 ppm).(1) Hexavalent chromium concentrations are rarely reported, but since steel is manufactured in an oxidizing environment, and at high temperatures, and since it is the purpose of the pickling operation to remove residual metal oxides from the steel surface, it is expected that the pickling liquor will, in fact, contain significant amounts of hexavalent chrome.

Approximately 40% of the mills utilizing the sulfuric acid pickling process discharge these and other pickling wastes after treatment to a receiving body of water. Another 45% of these mills have the spent pickle liquor hauled off-site by private contractors. Outside contract disposal services generally neutralize spent pickle liquors in unlined lagoons.(2) The remaining 15% of the sulfuric acid pickling mills either utilize deep well disposal, engage in acid recovery, or discharge the treated waste to Publicly Owned Treatment Works (POTWs) along with other pickling wastes which have undergone varying degrees of treatment. Disposal practices of combination acid pickling mills and hydrochloric acid pickling mills are known to be similar to those used by sulfuric acid pickling mills.(1)

IV. Hazardous Properties of the Waste

The pickling process requires highly acidic solutions; hence, spent pickle liquors are highly corrosive, with a

pH of less than 2 (see Table 2). Therefore, this waste meets the corrosivity characteristic (§261.22) and is thus defined as hazardous. In addition, Agency data indicate that significant levels of the toxic metals lead and chromium are found in the spent pickle liquor (see Table 2 below).

Table 2
Typical Concentrations of Lead and Chromium in
Spent Pickle Liquors(mg/l)

<u>Parameter</u>	<u>H₂SO₄Bath</u>	<u>HCL Bath</u>	<u>Mixed Acid Bath</u>
pH	1.0-2.0	1.0-4.5	1.3-1.5
Cr	26-269	2-37	3300-4250
Pb	ND*-2	2-1550	1-4

*ND=Nondetectable

Source: Reference 1

Based on the higher concentration levels listed in Table 2 for chromium and lead (4250 and 1550, respectively), if only .12% of the chromium (if hexavalent) and .33% of the lead leach from the spent pickle liquor, this amount would exceed the permissible concentrations of chromium and lead in the EP extract.* Since the spent pickle liquor is a highly acidic solution, these toxic metals are readily available to migrate into the environment, as they are more

*The concentrations of lead and chromium in these wastes can vary, depending upon the composition of the raw materials used to manufacture the steel and the particular type of steel pickled.

soluble in acidic environments.(6) In particular, since trivalent chromium has only slight solubility in acids and the hexavalent form is extremely soluble, the chromium in the acid leachate will be overwhelmingly hexavalent. Thus, disposal of this waste in landfills or lagoons, if improperly managed, is likely to lead to the migration of harmful constituents into the environment and pose a substantial hazard via a groundwater exposure pathway.

Possible Types of Improper Management and Available Pathways of Exposure

As shown above, disposal of spent pickling liquors creates the potential for leaching of the toxic metals (presumably hexavalent) chromium and lead to groundwater, a common source of drinking water. In addition, improper storage and/or disposal of spent pickling liquor poses potential hazards stemming from the high acidity of the wastes. In particular, if not segregated in a landfill, spent pickle liquors can extract and solubilize toxic contaminants (especially metals) from other wastes disposed in the landfill. In view of the low solubility of most trivalent chromium compounds, and the high solubility of most hexavalent forms (see Attachment I), the leachate is expected to contain predominately the hexavalent form. If not stored in special containers, pickle liquors can, over time, corrode the containers, resulting in leakage and potential acid burns to individuals who may come in contact with the waste.

Transportation of about 45% of the spent pickle liquors generated to off-site disposal facilities before

neutralization (see p.4, above) increases the likelihood of their causing harm to people and the environment. Improper containment of these wastes may result in their doing harm to individuals or to the environment during transportation to their designated destination. Moreover, mismanagement of these wastes during transportation may result in their not reaching their designated destination at all, thus making them available to do harm elsewhere.

Once released from the matrix of the waste, lead and (presumably hexavalent) chromium can migrate from the disposal site to ground and surface waters used as or constituting potential drinking water sources. Present practices associated with landfilling or impounding the waste may be inadequate to prevent such an occurrence. For instance, selection of disposal sites in areas with permeable soils can permit contaminant-bearing leachate from the waste to migrate to groundwater.

An overflow problem might also be encountered if the liquid portion of the waste has been allowed to reach too high a level in the lagoon. Thus, a heavy rainfall could cause flooding which might reach surface waters in the vicinity.

In addition to difficulties caused by improper site selection, unsecure landfills in which wastes may be disposed of are likely to have insufficient leachate control practices. Available information, in fact, indicates that liners are not presently used in the landfilling or lagooning of these wastes.⁽¹⁾ There may be no leachate collection and treatment system to diminish leachate percolation through the wastes and soil

underneath the site to groundwater and there may be no surface run-off diversion system to prevent contaminants from being carried from the disposal site to nearby surface waters.

An additional regulatory concern is the huge quantities of these wastes generated annually. Spent pickle liquor is generated in very large quantities. The large quantities of this waste and the contaminants it contains pose a serious danger of polluting large areas of ground or surface waters. Contamination could also occur for long periods of time since large amounts of pollutants are available for environmental loading. Attenuative capacity of the environment surrounding the disposal facility could also be reduced or used up due to the large quantities of pollutants available.

V. Hazards Associated with Lead and Chromium

The lead and chromium that may migrate from the wastes to the environment as a result of such improper disposal practices are metals that persist in the environment in some form and, therefore, may contaminate drinking water sources for long periods of time. Hexavalent chromium is toxic to man and lower forms of aquatic life. Lead is poisonous in all forms. It is one of the most hazardous of the toxic metals because it accumulates in many organisms, and its deleterious effects are numerous and severe. Lead may enter the human system through inhalation, ingestion or skin contact.

Improper management of these wastes may lead to ingestion of contaminated drinking water. Aquatic toxicity has been observed at sub-ppb levels. Additional information on the adverse health effects of chromium and lead can be found in Appendix A.

The hazards associated with lead and chromium have been recognized by other regulatory programs. Lead and chromium are listed as priority pollutants in accordance with §307(a) of the Clean Water Act of 1977. National Interim Primary Drinking Water Standards have been established for both parameters. Under §6 of the Occupational Safety and Health Act of 1970, a final standard for occupational exposure to lead and chromium has been established and promulgated in 19 CFR 1910.1000.(8,9) Also, a national ambient air quality standard for lead has been announced by EPA pursuant to the Clean Air Act. (8) In addition, final or proposed regulations of the States of California, Maine, Massachusetts, Minnesota, Missouri, New Mexico, Oklahoma and Oregon define chromium and lead-containing compounds as hazardous wastes or components thereof.(10)

VI. Damage Incidents*

These damage incidents are attributable to the improper disposal of spent pickle liquor. They are just a few examples of the damage which may result if these wastes are mismanaged.

*Draft Environmental Impact Statement for Subtitle C, Resource Conservation and Recovery Act of 1976, Appendices-Reference 7.

- In Washington County, Pennsylvania, leachate from a landfill has entered the groundwater and has contaminated a farmer's well and spring a half mile away. The landfill accepts sludges containing heavy metals and poorly neutralized pickle liquor from steel mills.
- In April, 1975. An employee in York County, Pennsylvania, siphoned wastes from a company's settling pond into a storm drain emptying into a fishing creek. The acidity of the drained wastes caused a fish kill in the creek. The waste and sludge in the ponds were spent pickle liquors which had allegedly been neutralized. The sludge is to be hauled to a landfill and the lagoons are to be lined.

References

1. U.S. EPA. Draft development document for the proposed effluent limitations guidelines and standards for the iron and steel manufacturing point source category; sulfuric acid pickling subcategory, hydrochloric acid pickling subcategory. v.8. EPA No. 440/1-79-024a. November, 1979.
2. U.S. EPA. Office of Solid Waste. Assessment of industrial hazardous waste practices in the metal smelting and refining industry. v.3. EPA No. SW-145c3. NTIS PB No. 276 171. April, 1977.
3. Waste characterization data from the State of Illinois EPA, as selected from State files by U.S. EPA/OSW on 3/14/79 and 3/15/79.
4. Waste characterization data from the State of Pennsylvania Department of Environmental Resources, Division of Solid Waste Management, March 20, 1978, as selected from State files by U.S. EPA/OSW, on 1/4/79 and 1/5/79.
5. Not used in text.
6. Pourbaix, M. Atlas of electrochemical equilibria in aqueous solutions. Pergamon Press, London. 1966.
7. Appendix J--Hazardous waste incidents, Draft Environmental Impact Statement for Subtitle C, RCRA. January 1979, as synopsised from Office of Solid Waste, Hazardous Waste Management Division; Hazardous Waste Incidents, unpublished open file data. 1978.
8. U.S. Department of the Interior, Bureau of Mines. Mineral commodity summaries. 1979.
9. NIOSH. Registry of toxic effects of chemical substances. U.S. Department of Health, Education and Welfare, National Institute for Occupational Safety and Health. 1977.
10. U.S. EPA States Regulations Files. January, 1980.
11. Not used in text.

Attachment I

SOLUBILITY AND ENVIRONMENTAL MOBILITY

CHARACTERISTICS OF CHROMIUM COMPOUNDS

The tripositive state is the most stable form of chromium. In this state chromium forms strong complexes (coordination compounds) with a great variety of ligands such as water, ammonia, urea, halides, sulfates, amines and organic acids.(a,b) Thousands of such compounds exist. This complex formation underlies the tanning reactions of chromium, and is responsible for the strong binding of trivalent chromium by soil elements, particularly clays.(c,d)

At pH values greater than about 6, trivalent chromium forms high molecular weight, insoluble, "polynuclear" complexes of $\text{Cr}(\text{OH})_3$ which ultimately precipitate as $\text{Cr}_2\text{O}_3 \cdot n\text{H}_2\text{O}$. This process is favored by heat, increased chromium concentration, salinity and time.(a) These chromium hydroxy complexes, formed during alkaline precipitation treatment of Cr-bearing wastes, are very stable, and relatively unreactive, because the water molecules are very tightly bound. In this form, Cr is therefore resistant to oxidation. Three acid or base catalyzed reactions are responsible for the solubilization of chromium hydroxide:

Reaction	Keq.(18)	Cr(III) Concentration Calculated from keq (mg/l)		
		pH5	pH6	pH7
1. $\text{Cr(OH)}_3 + 2\text{H}^+ \rightleftharpoons \text{CrOH}^{++} + 2\text{H}_2\text{O}$	10^8	520	5.2	0.052
2. $\text{Cr(OH)}_3 \rightleftharpoons \text{Cr}^{+3} + 3\text{OH}^-$	6.7×10^{-31}	35	0.035	i*
3. $\text{Cr(OH)} \rightleftharpoons \text{H}^+ \text{CrO}_2^- + \text{H}_2\text{O}$	9×10^{-17}	1	1	1

*i = <0.001 mg/l

It is apparent from these figures that, in theory, trivalent chromium could leach from sludges to some extent. Such solubilized chromium, however, is unlikely to contaminate aquifers. It is complexed with soil materials, and tenasiously held.(a,d) Little soluble chromium is found in soils.(a,e) If soluble trivalent chromium is added to soils it rapidly disapperas from solution and is transformed into a form that is not extracted by ammonium acetate or complexing agents.(c,e) However, it is extractable by very strong acids, indicating the formation of insoluble hydroxides.(d,e) Thus: above pH5, chromium(III) is immobile because of precipitation; below pH4, chromium(III) is immobile because it is strongly absorbed by soil elements; between pH 4 and 5 the combination of absorption and precipitation should render trivalent chromium quite immobile.(c,d)

In contrast, hexavalent chromium compounds are quite soluble, and hexavalent chromium is not as strongly bound to

A/2

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soils.(c,d) Hexavalent chromium remains as such in a soluble form in soil for a short time, and is eventually reduced by reducing agents if present.(e,f) As compared with the trivalent form, hexavalent chromium is less strongly adsorbed and more readily leached from soils(d) and thus, is expected to have mobility in soil materials.(d)

References

- a. U.S. EPA, Reviews of the Environmental Effects of Pollutants; III Chromium. ORNL/EIS-80; EPA-600/1-78-023; May 1980.
- b. Transition Metal Chemistry, R.L. Carlin, ed. Marcel Dekker, New York. 1965; Volume 1.
- c. Bartlett, R.J. and J.M. Kimble. Behavior of Chromium in Soils: I Trivalent Forms. J. Environ. Qual. 5: 379-383: 1976.
- d. Griffin, R.A., A.K. Au, and R.R. Frost. Effects of pH on adsorption of chromium from landfill leachate by clay minerals. J. Environ. Sci. Health A12(8): 430-449:1977.
- e. U.S. EPA. Application of Sewage Sludge to Cropland; Appraisal of Potential Hazards of the Heavy Metals to Plants and Animals. EPA 430/9-76-013. NTIS PB No. 264-015. November, 1976.
- f. Bartlett, R.J. and J.M. Kimble. Behavior of Chromium in Soils: II Hexavalent Forms. Ibid. 5:383-386. 1976.

Response to Comments - Spent Pickle Liquor and Sludge
from Lime Treatment of Spent Pickle Liquor in Steel
Finishing Operations

Spent Pickle Liquor from Steel Finishing Operations (K062)

One commenter requested that this particular listing be deleted, in its entirety, from the hazardous waste regulations. In the comment, it is pointed out that spent pickle liquor is widely used to precipitate phosphorous from wastewater in publicly owned treatment plants (POTW's). The commenter also states that pickle liquor is used for sludge conditioning. These practices have been the subject of numerous demonstration grants, research reports, major technology transfer promotions, etc., and the commenter argues that if pickle liquor is designated as hazardous, then many POTW's may be considered unrealistically to be storers and treaters of hazardous waste. Finally, the commenter indicates that in several literature reviews, including several EPA reports, it is stated that inorganic coagulants, precipitants and sludge conditioners, such as pickle liquor, contribute to the removal and precipitation of various components from wastewaters that were originally present from other natural sources and are not in themselves a significant source of toxic heavy metals such as Cr and Pb.

The short answer to this comment is that POTW's using spent pickle liquor in treatment operations are deemed to have

a permit by rule, subject to the conditions specified in §122.26(c) (45 FR 33435). Thus, the commenter's principal concerns have already been dealt with.

Moreover, the comment is misplaced in that it fails to challenge the Agency's determination that spent pickle liquor is hazardous. The Agency continues to stand on its finding that this waste stream is indeed hazardous. We note in this regard, that the American Iron and Steel Institute, whose members are among the principal generators of this waste, does not challenge the listing.

It may be that the commenter is arguing that the reuse of spent pickle liquor should not be deemed hazardous waste management.

As discussed in the preamble to the Part 261 regulations promulgated on May 19, 1980 (45 FR 33091-33095), the Agency has concluded that it does have jurisdiction under Subtitle C of RCRA to regulate waste materials that are used, reused, recycled or reclaimed. Furthermore, we reasoned that such materials do not become less hazardous to human health or the environment because they are intended to be used, reused, recycled or reclaimed in lieu of being discarded. Although the materials after being recycled and reclaimed may not pose a hazard, the accumulation, storage and transport of a hazardous waste prior to use, reuse, recycle or reclamation will present the same hazard as they would prior to being discarded. In addition, the act of use, reuse, recycling or

recclamation, in many cases, poses a hazard equivalent to that encountered if the waste were discarded. Thus, the Agency believes it has a strong environmental rationale for regulating hazardous wastes that are used, reused, recycled or reclaimed.

For the particular wastes at issue, the Agency found that this waste for most or all of its existence prior to being recycled is stored in tanks or drums. If not stored in special containers, pickle liquors can corrode the containers, resulting in leakage and potential acid burns to individuals who may come in contact with the waste. Consequently, the waste must be considered a hazardous waste in this environment.

Sludge from Lime Treatment of Spent Pickle Liquor from Steel Finishing Operations

A number of comments were received which objected to the listing of sludge from lime treatment of spent pickle liquor from steel finishing operations as a hazardous waste. The commenters argue that the Agency's rationale for listing this particular waste is objectionable both on procedural grounds and on technical grounds. With respect to the procedural arguments, the commenters point out that the Agency has failed to articulate the bases for its conclusion, effectively precluding meaningful comment. In addition, they argue that in analyzing the listing background document, the Agency has ignored its own standards and procedures for determining hazardousness; and thus, they claim that the Agency

has violated fundamental principles of administrative law, and that its decision to list sludge from lime treatment of spent pickle liquor is unlawful.

On the technical side, the commenters argue that the Agency has relied on inadequate or inappropriate data to reach its conclusions, and that to the extent that the conclusion is discussed, none of the assertions are adequately substantiated in the listing background document or references cited therein. For example, the commenter points out that the listing background document does not show the specific data or go through the calculations from which EPA derived the "average" chromium and lead concentrations in the sludge. The most important objection, however, relates to the use of a single leaching test, using the Illinois EPA extraction procedure, to make the statement that leaching of chromium and lead has been shown to occur. The commenters took special exception to the use of the Illinois EPA extraction procedure, a test which calls for the addition of an unlimited amount of acid to maintain a pH of 4.9 to 5.2, rather than the U.S. EPA extraction procedure which calls for maintenance of acid conditions, but allows only limited acid addition. To refute the leaching argument, one commenter submitted data on leachate tests carried out by a number of steel companies using the Agency's extraction procedure (see Table 1).

Table 1
Leachate Analysis Using EPA's Extraction
Procedure on Sludge from the Lime Treatment
of Spent Pickle Liquor

Sludge Sample	Cr(mg/l)	Pb(mg/l)
6	0.002	0.006
12	0.002	0.004
28	0.002	0.002
1	0.05	0.15
2	0.03	0.19

The commenter felt that these data indicate that the sludge from lime treatment of spent pickle liquor is not hazardous because all concentrations are well below EPA's promulgated limit for classification as a hazardous waste. Therefore, the commenters recommended the sludge from lime treatment of spent pickle liquor be deleted from the list of hazardous waste.

The Agency strongly disagrees with the commenter that the Agency has ignored its own standards and procedures for determining the hazardousness of the waste. This particular waste (K063) was assigned a "T" hazard code, indicating a toxic waste. The listing criteria for toxic wastes provide that a waste will be listed as hazardous where it contains any of a number of designated toxic constituents, unless after consideration of certain specified factors (261.11(a)(3)), the Agency concludes that the waste does not meet part [B] of the statutory definition of hazardous waste.

In waste K063, the Agency identified two toxic constituents (chromium and lead) in the waste. The Agency then evaluated the toxicity of this waste based on a number of the factors cited in §261.11(a)(3) (i.e., concentration of the constituent in the waste, potential of the constituents to migrate from the waste, the persistence of the toxic constituents, plausible types of improper management, etc.). Based on the available data, the Agency felt that sludge from lime treatment of spent pickle liquor may present a substantial hazard to human health or the environment, if improperly managed. With respect to the commenters objection to consideration of data derived from use of the Illinois EPA extraction procedure, the Agency strongly believes that any extraction testing, whether used by the States, industry or Federal government, may be considered by the Agency in evaluating the migratory potential of the toxic constituents in the waste. §261.11(a)(3)(iii) does not require the Agency to use the EP but rather to assess "...the potential of the constituent or any toxic degradation product of the constituent to migrate from the waste into the environment under the types of improper management considered in paragraph (a)(3)(vii) of this section." For this particular waste, the Illinois EPA extraction procedure may be most appropriate for determining the potential mobility of the heavy metals in the waste because of the potential for this waste to be mixed with other acid wastes or the potential for the spent pickle liquor to be poorly neutralized (see section VI of the background document).

However, in recognition of the commenter's data, the Agency has decided to delete this waste from the interim final hazardous waste list, and to rely on the provisions of §261.3 to bring these wastes within the hazardous waste management system. Since these lime treatment sludges are generated from the treatment of a listed hazardous waste (K062), they are considered to be hazardous wastes (§261.3(c)(2)) and will remain as hazardous unless and until they no longer meet any of the characteristics of hazardous waste and are delisted (§261.3(d)(2)). The Agency does not believe that sufficient information has been submitted to exclude totally the waste from the hazardous waste regulations, however the Agency would consider an industry-wide rulemaking petition to exclude these wastes from Subtitle C jurisdiction if the industry presents representative data showing the wastes are not hazardous. It should be noted that the lime treatment itself will require a hazardous waste management permit, since it constitutes treatment of a hazardous waste.